In Situ Observation of Reversible Single-Crystal-to-Single-Crystal Apical Ligand Exchange Reaction in a Hydrogen-Bonded 2-D Coordination Network

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Supporting information (5 pages)
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1. The Synthesis of 1

2,3-bis(2-hydroxyethoxy)-1,4-bis(4-pyridyl)benzene: A solution of NaOH (4.0 g, 100 mmol) in H₂O (100 mL) was added in portions to stirred mixture of 1,4-diiodo-2,3-dihydroxybenzene¹ (7.24 g, 20 mmol) and 2-bromoethanol (12.4 g, 100 mmol) in H₂O under N₂ (Scheme 1). The temperature of the reaction mixture should be below 30 °C. When the addition was completed, the temperature was raised to 90 °C, the mixture was stirred for 3 h. After cooling of the mixture to 40 °C, H₂SO₄ (0.3 mL) was added. The resultant mixture was stirred at 25 °C for 4 h and colorless powder was separated by filtration, dried, and purified by recrystallization from AcOEt to yield 2,3-bis(2-Hydroxyethoxy)-1,4-bis(4-pyridyl)benzene as colorless powder (4.15 g, 46%).

1: A mixture of 2,3-bis(2-Hydroxyethoxy)-1,4-bis(4-pyridyl)benzene (2.12 g, 5 mmol), 4-pyridyloboronic acid ester (2.56 g, 12.5 mmol), K₃PO₄ (7.80 g, 37.5 mmol) and [Pd(PPh₃)₄] (300 mg) in dioxane (100 mL) was refluxed under an Ar atmosphere for 2 d (Scheme 1). After removal of the dioxane, the residue was purified by flash chromatography (MeOH/CHCl₃, 1/20) to give 1 as colorless powder (1.06 g, 60%).

¹H NMR (500 MHz, CDCl₃, 300 K): δ = 8.68 (d-like, J=5.0Hz, 4H, PyHα), 7.56 (d-like, J=5.0Hz, 4H, PyHβ), 7.27 (s, 2H, ArH), 3.89-3.87 (m, 4H, CH₂a), 3.72 (m, 4H, CH₂b), 2.06 (br, 2H, OH); ¹³C NMR (125 MHz, CDCl₃, 300 K): δ = 150.3 (Cq), 149.9 (CHα), 145.3(Cq), 134.2 (Cq), 126.1 (CHγ), 123.8 (CHβ), 75.9 (CH₂a), 61.4 (CH₂b).

2. A similar square grid coordination network which does not possess an ethylene glycol chain on the ligand

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\begin{align*}
\text{N} & - \text{N} \\
\text{4} & \text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \\
\rightarrow & \quad \{[\text{Co(II)(4)}_2(\text{H}_2\text{O})_2]\text{(NO}_3\text{)}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeOH}\}_n (2)
\end{align*}
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Figure S1. (a) Square-grid network of 5. (b) Two-layer stack of 5.

A bifunctional ligand of 4 having no ethylene glycol chain was used for the complexation.\(^2\) Single crystals of complex 5 was synthesized by layering a MeOH solution of Co(NO\(_3\))\(_2\) • 6H\(_2\)O onto a toluene solution of 4. After the solution was allowed to stand for a week, the crystals formed were isolated by filtration in 53% yield (eq.2). X-ray crystallographic analysis reveals the square grid network structure of \{[Co(II)(4)_2(H_2O)_2](NO_3)_2 • 2H_2O • 2MeOH }\_n (5). The crystal packing of 5 is similar to that of 2 (Figure S1).

Crystal data for 5: monoclinic, \(\text{Cc}, \ a = 16.8603(19) \ \text{Å}, \ b = 15.6965(18) \ \text{Å}, \ c = 15.2546(17) \ \text{Å}, \ \beta = 112.062(2)\(^\circ\), \ V = 3741.5(7) \ \text{Å}^3, \ Z = 4, \ T = 80 \ \text{K}, \ D_{\text{calc}} = 1.406 \ \text{gcm}^{-3}, \ \mu = 0.531 \ \text{mm}^{-1}, \ \text{Final } R_1 (I>2\sigma(I))=0.0666, \ wR_2 (\text{all data}) = 0.1949, \ \text{GOF}= 1.137.

CCDC-250611 (5) contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (t44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Comparison by X-ray analysis: Whereas 2 kept its crystallinity even at high temperature (<150 °C), crystal 5 gradually deteriorated above room temperature and no longer diffracted at 60 °C.

Comparison by thermogravimetric analysis: As shown in Figure S2, 2 showed much higher thermal stability than 5 (decomposition temperature: 2, 220 °C; 5, 170 °C).

Figure S2. TG curve of 2 (green) and 5 (red) measured in N₂ (heating rate is 2 °C/min)
3. TG/DSC curve of 2

Figure S3. TG/DSC curves of 2 measured in N\textsubscript{2} (heating rate is 2 °C /min)